



Description of EP0545043

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The invention relates to a base paper for photographic supports.

When Rohpapier for the production of photographic supports becomes a wet-solid, dimension-stable paper made, which must be free of photo-chemical and mechanical impurities. The interior gluing paper must be always so aligned that it works against the pouring effect with the aqueous post treatment.

A resin coating prevented additional that with developing chemicals and water penetrate into the Rohpapier.

As pulp for the Rohpapier so-called therefore up to now only particular pulps become. Photo celluloses used, which exhibit a special degree of purity. Here it concerns bleached sulfite or sulfate pulps out of needle and hardwood. Usually for these pulps used bleaching processes is the polluting chlorine bleaching process. In the last years a technological change carries out itself to "pollution free" bleaching agents in the range of the bleach. Like that is z. B. in the Japanese disclosure writing J 63-303 191 a photographic support described, whose production a oxygen-bleached pulp becomes used.

Effort to preserve the natural raw material resources and use more pollution free manufacturing processes, extended is to become also on other ranges.

It is therefore object of the invention suggesting a base paper for photographic supports that not only all requirements conventional for photographic base papers, like z. B. Smooth one, surface after the processing in photographic baths, stiffness, interlaminar strength, photo-chemical neutrality opposite photosensitive emulsions, but also from ecological reasons of the requirement after a better utilization of raw material and a more pollution free production organization, existing in the public, becomes fair.

This object becomes dissolved by the fact that becomes used for the production of the basis paper a pulp, which contains recycling stuff between 5 and 100%.

The base paper can consist thus complete of recycling stuff, in addition, of a mixture of recycling stuff with standard cellulose or photo cellulose.

With the term recycling stuff becomes a stuff referred, which from waste paper by suitable and known material processing routes generated becomes.

The used waste papers become after groups of sorts as well as classified within the groups of sorts characterized and (waste paper list German standard places and her qualities, dressing of German paper factories, valid starting from 1.1.89).

In a special embodiment of the invention the Papierkern can contain also a photo and/or a standard cellulose.

The bottom term photo cellulose is a pulp meant, which has itself for the photo paper manufacturers regarding mechanical and photo-chemical impurities qualified, i.e. that the dirt particle level  $1.7 \text{ mm} < 2 > /m < 2 >$  and the level of the iron and copper impurities 30 Punkte/kg pulp deleterious for the photographic emulsions not to exceed may.

With a so-called. The respective values somewhat higher, may however the boundary 3.5 mm of  $2 / m < 2 >$  are appropriate< for standard pulp> and 50 Punkte/kg pulp do not exceed.

The Papierkern can using dimerisieren alkyl ketenes in the neutral pH range common with cationic resins, like e.g. cationic PP polyamine epichlorohydrin resin, kationische polyacrylamides, cationic starch or polyethylenimines, to be glued (neutral gluing). Alkyketendimere with different prolonged alkyl chains used can become. A particularly preferred dimerisieren alkyl ketene exists to at least 50% of Behenylketen or another alkyl ketene with more than 18 C-atoms in the alkyl radical. The hydrocarbon group of the ketene can contain also ring structures or C=C-Doppelbindungen.

For the neutral gluing also different reactive sizing agents can, like z. B. epoxidized fatty acid amides, fatty acid anhydrides or alkyl succinic acid anhydride, used become.

In another embodiment of the invention the Papierkern is glued using non reactive sizing agents like higher fatty acids or fatty acid salts in an acidic pH range from 3.5 to 5 common with polyvalent metal ions in form of a salt such as aluminium sulfate, aluminium chloride or sodium aluminate (acidic gluing). The fatty acids can be saturated or unsaturated. They contain 14 to 20 C-atoms and are z. B. Palmitic acid, stearic acid or oleic acid. Preferred one becomes stearic acid as well as their salts, z. B. Sodium stearate.

In other embodiments two or more hydrophobierende sizing agents are contained of the invention in the paper. Reactive sizing agents with non reactive sizing agents can become combined. A preferred combination is for example a combination from alkyl ketene dimer and fatty acid, in addition, a combination from epoxidized fatty acid amide and fatty acid is in the scope of the invention possible.

Prepared according to invention base papers can contain all otherwise still conventional Zusatzstoffe such as white

pigments, dyes, color pigments, fillers and other aids.

In an other embodiment of the invention the Papierkern beside an interior gluing additional is provided with a Oberflächenleimung, the z. B. of a strengthening or a polyvinyl alcohol line consists, which becomes from aqueous solution

- ▲ <sup>1</sup>with a known order procedure applied on the paper web. The order quantity amount to 0.5 to 10 g/m<sup>2</sup>, preferably 1 to 4.5 g/m<sup>2</sup>.

The Papierkern according to invention can become then on at least a side with a synthetic resin layer coated.

In a special embodiment of the invention the Papierkern according to invention with a synthetic resin layer is coated, by UV and/or. Electron beams hardened becomes. By means of radiate solidified coat preferably contain beside the bonding agent pigment and has a basis weight from 5 to 40 g/m<sup>2</sup>. The bonding agent essentially consists of such cloths, who contain CC double bonds. Preferred pigments are white pigments such as TiO<sub>2</sub>, BaSO<sub>4</sub>, ZnO, CaCO<sub>3</sub> and also color pigments.

The synthetic resin layer applied on the Papierkern of at least a side can become also in aqueous dispersion applied. As bonding agents natural or synthetic polymeric compounds can become used. Additional one to the bonding agent knows the layer still different additives such as white pigments, dyes, hardening agents among other things contained.

The Papierkern according to invention can be provided by at least a side also with a synthetic resin layer, which becomes applied by means of extrusion coating. The for this thermoplastic resins are preferably polyolefins, in particular polyethylene (HDPE, LDPE), ethyl alpha - olefine copolymers (LLDPE) or polypropylenes. The polyolefin coat knows a light reflective weisspigment as well as if necessary. Color pigments, optical brighteners, antistatic agents, dispersion aids and other additions contain. The order quantity of the coat amounts to 5 to 50 g/m<sup>2</sup>. Preferred pigments are titanium dioxides of the rutile or Anatase type, those in an amount from 5 to 20 Gew.-% used become.

Surprisingly it put you out that the photographic base papers concerning the required properties, prepared using recycling stuff, like z. B. Surface quality, edge penetration photographic liquids or photo-chemical neutrality, with photographic base papers, which become prepared using photo celluloses, is more comparable.

The invention becomes explained on the basis the subsequent examples.

Except the waste paper places described in example 1 the recycling stuff also different kinds examined were more insertable found and likewise than.

#### Example 1

A fibrous material mixture corresponding table 1 became milled with a Stoffdichte of 4% up to a freeness of 35 DEG SR. The fibrous material suspension became then neutral sizing agents

(Thick matter: 2.5% TiO<sub>2</sub>, 0.057% white toner, 1.5% anionic starch

Thin material: 0.7% polyamide/polyamine epichlorohydrin resin,

0.5% alkyl ketene dimer

0.11% epoxidized fatty acid amide)

added and from on approximately 1.2 Gew.-% diluted suspension in known manner approx. 170 g/m<sup>2</sup> heavy base papers made. The papers were upper-flat-glued in also known manner with a solution, the 4.4 Gew.-% oxidized starch, 0.03% white toner and 21 g/l NaCl contained. EMI7.1

#### Example 2

Analogous example 1 became approx. 170 g/m<sup>2</sup> heavy base papers prepared.

The composition of the fibrous material mixture is in table 2 indicated.

<tb> < TABLE> 1< Tabelle 2 Columns=4

<tb> Composition of the fibrous material mixture in Gew.-%

<tb>

<tb> Head Col 1: Kind of fibrous material

<tb> Head Col 2: 2.1

<tb> Head Col 3: 2.2

<tb> Head Col 4: 2.3

<tb> hardwood sulfate cellulose (photo cellulose)< September> 90< September> 50< September> -

<tb> recycling stuff D< September> 10< September> 50< September> 100

<tb>< /TABLE>

#### Example 3

A mixture from 30 Gew.-% recycling stuff kind F and 70 Gew.-% hardwood sulfate cellulose became milled with a Stoffdichte of 4% up to a meal reason of 35 DEG SR. The pulp suspension became then sizing agents (thick matter: 0.04 Gew.-% white toner, 0.35 Gew.-% anion. Polyacrylamide, 1.55 Gew.-% Stearin, 0.8 Gew.-% alum, 0.54 Gew.-% kat. Polyacrylamide; Thin material: 0.41 Gew.-% polyamide/polyamine epichlorohydrin resin) with pH = 4.5 added.

From on approximately 1.2 Gew.-% diluted suspension became in known manner approx. 170 g/m<sup>2</sup> heavy base paper made. The paper was surface-glued in also known manner with a solution, the 3.45 Gew.-% polyvinyl alcohol, 4 Gew.-% CaCl<sub>2</sub> x H<sub>2</sub>O and 0.53 Gew.-% white toner contained.

#### Comparison example 1

A mixture from 100 Gew.-% Hardwood sulfate cellulose (photo cellulose) became milled with a Stoffdichte of 4% up to a freeness of 35 DEG SR. The pulp suspension became then neutral sizing agents 1 added as in the example and approx. 170 g/m<sup>2</sup> heavy base papers prepared.

Analogous example 1 the papers were surface-glued.

#### Comparison example 2

A pulp suspension in accordance with comparison example 1 sizing agents became as approx. in the example 3 added and 170 g/m<sup>2</sup> heavy base papers prepared.

By the corresponding examples and comparison examples made paper samples a part uncoated was left and tested, another part were submitted in each case reciprocally in known manner with polyethylene coated and in this form of an examination. In the scope of the invention the appended listed test methods were consulted for the evaluation.

#### Surface number (OZ)

The examination made at uncoated paper samples after the testing method described in DE-OS 34 26 782. The per high surface number, all the poorer is the surface quality. The surface numbers conventional for the base papers prepared using photo celluloses are during neutral gluing within the range of 140 - 190 and with acidic gluing within the range of 90 - 150.

#### Edge-penetrate from developer (KE)

The paper samples coated with polyethylene were cut and in the required sample-large for 14 minutes in a commercial Color Entwicklerbad (T = 30 DEG C) immersed. After intermediate splash-down, treatment with commercial fixing solution and subsequent splash-down the patterns dried became and with a measuring magnifying glass the depth of penetration (in mm) of the developer solution at the cut edge measured. The zone of the developer penetration is to be recognized as more or less brownish discoloured edge strip in the transmitted light. The number data in the subsequent tables are averages from in each case 6 individual measurements.

For on conventional wise prepared base papers the conventional worth the edge penetration may not 0.5 mm exceed.

#### Structure firmness

The structure firmness (inner strength) became certain after TAPPI RC 308 with a Scott bond interlaminar strength examiner (Internal bond Impact tester Model B). The number data in the subsequent tables are in each case averages from 5 individual measurements.

The values of the structure firmness conventional for the base papers prepared on conventional manner lie during neutral gluing within the range of 150 to 300 ft.lb/sq.in and with acidic gluing in the range 110 to 150 ft.lb/sq.in. The ever high value, all the larger is the inner strength of the paper.

#### Photo-chemical properties

For the examination of the photo-chemical properties 4 various photographic emulsions were consulted, which exhibit different photosensitivities. Such an emulsion is for example in EP-OS 0023668 described.

For this the test emulsion becomes with the help of a casting machine applied and dried on the base paper. Afterwards the coated pattern becomes a middle grey clay/toner exposed, developed and fixed. The judgment with notes (1 - 6) made visual due to a comparison with a collecting main, whereby the note 1 stands for "very good" and the note 6 for "poor".

The results of all described examinations are in the tables 3 and 4 assembled. As from the tables apparent, lie the test results of the base papers prepared using recycling stuff in the range conventional for conventional base papers prepared using photo celluloses. EMI12.1 EMI13.1